PATENT SPECIFICATION

(11) 1401673

(21) Application No. 36973/72 (22) Filed 8 Aug. 1972

(31) Convention Application No. 2139774 (32) Filed 9 Aug. 1971 in

(33) Germany (DT)

(44) Complete Specification published 30 July 1975

(51) INT CL² F01N 3/15 B01D 53/34 F01N 3/16

(52) Index at acceptance

B1F 100 D1B

C1A S171 S181 S183 S186 S18Y S201 S204 S211 S215 S21X S31Y S23X S46X S46Y S471 S491 S601 S60X S60Y SA

(19) THE PATENT OFFICE LONDON

(54) CATALYTIC EXHAUST SYSTEM FOR INTERNAL COMBUSTION ENGINES

(71) We, VARTA AKIENGESELLSCHAFT, a German Company, of 600 Frankfurt/Main, Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The invention relates to a catalytic exhaust system for an internal combustion engine, particularly the engine of a motor vehicle.

Legal provisions require or will in future require that the content of noxious substances, such as carbon monoxide, nitrogen oxides and unburnt hydrocarbons in the exhaust gases of motor vehicles propelled by internal combustion engines must not exceed a determined maximum amount. Since the quantities of noxious substances produced by an engine vary with the conditions under which the engine is operated, the exhaust gas has to be subjected to an aftertreatment for the decomposition of the noxious substances.

It has been proposed to subject the exhaust gases to a catalytic aftertreatment. For this purpose, the hot exhaust gas having a temperature of, for example, between 600° and 900°C is fed into an exhaust-gas reactor in which it is initially contacted with a bed of a reducing catalyst. The purpose of that catalyst bed is, with the aid of the incompletely burnt hydrocarbons, to reduce the nitrogen oxides formed in the engine, the reduction generally leading to the formation of ammonia.

After air for combustion has been supplied, the exhaust gas is catalytically oxidised in a second bed provided in the exhaust-gas reactor. Water and carbon dioxides are formed as reaction products. Undesirable nitrogen oxides, however, re-form upon the combustion of ammonia. The reducing catalyst usually comprises platinum deposited on alumina or on a ceramic supporting body.

A $CuO \cdot Cr_2O_3$ catalyst is generally used for the oxidising bed. These catalysts are generally used in the form of a catalyst bed consisting of a loose heap of small cylindrical rods 2 mm. in diameter and 5 to 10 mm. in length.

Catalyst beds of the aforedescribed kind have the disadvantage of a poor thermal conductivity. In addition, they offered a substantial resistance to the flow of the gas through the bed. Finally, these catalyst beds physically degenerate, as if they had been ground in a ball mill, as a result of the vibrations of the vehicle. Dust is produced and this becomes entrapped in the bed, thus increasing the resistance thereof to flow of the exhaust gases therethrough.

According to the invention there is provided an exhaust system for an internal combustion engine, the exhaust system having a catalyst in the path traversed in use by exhaust gases, the catalyst comprising one or more of the metals nickel, cobalt, iron, copper, silver, gold, chromium, molybdenum and tungsten, each such metal having been obtained by subjecting an alloy of it with an alloying metal to leaching with an acid or alkaline solution to remove said alloying metal.

The invention further provides a method of reducing the content of noxious constituents in the exhaust gases of an internal combustion engine, which comprises passing the exhaust gases through the exhaust system and in contact with the said catalyst.

The catalyst metals obtained upon leaching out said alloying metal, generally aluminium, are examples of metals commonly referred to as Raney metals and that terminology will be used in the following description "(Raney" is a Registered Trade Mark).

We have found that the metals nickel, cobalt, iron, copper, silver, gold, chromium, molybdenum and tungsten in the Raney form have particularly good properties for the catalysis of exhaust gases. These Raney metals are produced by alloying one or more of

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them with a catalytically inactive metal, hereinbefore referred to as the alloying metal, and subsequently removing the catalytically inactive metal from the alloy by means of an alkaline solution or by means of an acid. The crystal lattice of the alloy is destroyed by this process; the metals which are insoluble in the leaching solution have to rebuild a new lattice. The building of the new lattice proceeds at the low temperature of the leaching process, below about 100°C, so that a catalyst having a substantially disordered lattice of a large internal surface area is obtained.

In the course of time a large number of Raney metals have been produced and tested as catalysts in various fields of technology. Raney nickel obtained by leaching out the aluminium from an alloy comprising 50 parts by weight of nickel and 50 parts by weight of aluminium by means of a caustic alkali is the best-known such catalyst. In one particular process of controlled activation, the Raney catalyst may be produced by an anodic polarisation of the alloy within the alkali solution.

The Raney nickel used for some processes may be additionally activated by oxidising it slowly while controlling the temperature. The catalyst may be considerably improved by a subsequent tempering at about 400°C in which part of the nickel hydroxide formed during leaching of the initial alloy in the alkali solution, is converted into a stable oxide.

It is known that at a temperature of only 650°C Raney nickel decomposes ammonia at a high speed into nitrogen and hydrogen. The capacity of Raney nickel to operate as a hydrogenation catalyst is also known.

It is known to use Raney silver as an oxidation catalyst in oxygen diffusion electrodes. The oxidation of carbon monoxide may also be catalysed by Raney chromium, Raney molybdenum, Raney tungsten and Raney copper. It is also known that the presence of iron in Raney nickel produces a specific catalytic action upon the nitrogen/hydrogen compound hydrazine, since it assists the decomposition of hydrazine with the formation of ammonia instead of the formation of nitrogen and hydrogen.

We have found that a Raney catalyst comprising an alloy of the metals nickel, copper and chromium, which is produced by leaching out aluminium from an alloy of the four metals, nickel, copper, chromium and aluminium, is a particularly suitable catalyst for the catalysis of exhaust gas. In the catalyst, part of the nickel may be replaced by iron, part of the chromium by molybdenum and tungsten and part of the copper by silver. The catalyst is suitable for use in the exhaust-gas system both for the reducing and for the oxidising part.

Raney metals may be obtained either in the form of a fine powder or in the form of a moulded or shape body of very low strength. The low strength is a result of the total disintegration of the crystal lattice of the initial alloy upon leaching and to the low lattice ordering tendency of the Raney metal at the temperature (below 100°C) of leaching. Accordingly, Raney metals possess very large specific internal surfaces of about 50 sq.m./gram. Raney metals are often pyrophoric, in which case they may be stabilised and rendered insensitive to air by the slow air oxidation hereinbefore referred to. In this stabilised condition, the individual particles of the Raney metal may be compressed into moulded bodies of tablet form. The moulded bodies thus obtained have, however, a very poor mechanical strength owing to the low tendency of the oxidised surfaces to be welded together.

For this reason, moulded bodies comprising a metallic supporting skeleton and a granular or particulate Raney metal embedded herein have previously been produced. Bodies of this kind are referred to by the term "double-skeleton catalysts" see British Specifications Nos. 806,644 and 1,160,872. The double-skeleton catalyst is produced by pressing and sintering or hot-pressing a mixture of particles of the Raney metal alloy or the Raney metal with a pulverulent metal.

These double-skeleton catalysts, which have a good mechanical strength and high electric and thermal conductivities, are particularly suitable for use in reactions in which the high energy concentration requires that large quantities of reaction heat per unit time be supplied or dissipated. It has been found to be advantageous for the strength and the conductivity of the catalyst to be further increased by pressing a layer of the double-skeleton catalyst itself onto a support which is in the form of a gauze, sieve or sheet of a metal of good thermal conductivity.

It has been found that in the catalysis of an exhaust gas, normally only a very thin layer of a depth of 0.2 mm. from the surface of the catalyst participates in the reaction. Therefore in moulded bodies the thickness of the catalyst layer is advantageously less than 0.5 mm. and is preferably substantially 0.2 mm. In a catalyst bed of spheroids of identical dimensions, for example 2 mm. in diameter only 60% of the catalytic material used participates in the reaction, the remaining 40% does not normally perform any useful function and merely reduces the volume available to the gas.

Again, normally only 40% of a cylindrical body of infinite length and 2 mm. in diameter takes part in the reaction, and the remaining 60% constitutes a dead volume. The mass and thermal capacity of the bed are accord-

ingly increased by the quantities of unused catalyst, and the time required for reaching the operating temperature is extended.

A very effective catalyst bed comprises equidistantly spaced discs having a thickness of 0.4 mm., over which the exhaust gas flows parallel with the surface of the discs. The thermal conductivity may be improved by providing catalyst layers of a thickness of about 0.2 mm. on both sides of a supporting body which is in the form of a foil or a gauze. A catalyst bed having advantages from the aspect of gas flow may be produced from such catalyst laminates by moulding the individual layers into roof-shaped or pyramidal layers which are transferred to the catalyst space to form a bed therein. The catalyst laminates may also be in the form of open-ended cylinders which can be packed into a column, in a manner similar to that adopted with Raschig rings, to provide a catalyst bed favourable to gas flow.

A catalyst bed may be obtained by packing undulating or zig-zag-shaped catalyst layers and flat catalyst layers one upon the other. The walls of the channels thus formed consist of catalytic material of optimum thickness with respect to the depth of penetration of the reaction.

The nine Raney metals, namely Ni, Co, Fe, Cu, Ag, Cr, Mo and W, and mixtures and alloys thereof are cheaper reduction and oxidation catalysts than the noble metals hitherto frequently used for the purification of exhaust gases; furthermore, owing to their metallic structure, their heat conductivity is superior to that of catalysts deposited on an inert support, such as alumina or porcelain.

The invention is illustrated in the following Example.

EXAMPLE

A catalyst pot having a length of 20 cm. and a diameter of 10 cm. was, in a series of tests, filled with equal volumes of different catalysts.

Each catalyst was in the form of strips having a length of about 20 cm. and a thickness of 0.4 mm., and a nickel-plated iron gauze sandwiched between catalyst strips was used as a support, the catalyst strips having been applied to both sides of the gauze by hot-pressing.

In order to facilitate drawing a comparison between the actions of the different catalysts, the exhaust gas of a conventional internal combustion engine, which supplied about 350 cubic metres of gas per hour at a temperature of about 850°C, was analysed. The exhaust gas had the following composition by volume:—

14% carbon dioxide
11% water
2% carbon monoxide
0.8% hydrogen
0.2% oxygen
0.05% ammonia
0.03% hydrocarbons
0.01% nitrogen oxides
the remainder being nitrogen

When the determination of the composition of the exhaust gas was complete, the catalyst pot was connected in the exhaust line at a position just beyond the exhaust outlet of the engine, and the shift in the volume percentage of carbon monoxide, ammonia and nitrogen oxides brought about by the several catalysts at an operating temperature of about 600°C was determined.

% by volume		Composition of the alloy % by weight	% CO	% NH_3	% NO_x
Value without catalyst			2	0.05	0.01
Catalyst					
(1)	Raney—Cu		0.9	0.007	0.013
(2)	„ —Ni		1.4	0.0003	0.0006
(3)	„ —Ni Fe	90/10	1.4	0.0003	0.0017
(4)	„ —Ni Cu	60/40	0.55	0.001	0.0022
(5)	„ —Ni Cu Fe	60/30/10	0.6	0.0007	0.0020
(6)	„ —Ni Fe Cr	70/10/20	1.1	0.0003	0.0014
(7)	„ —Ni Cu Ag	90/8/2	0.9	0.0006	0.0010
(8)	„ —Ni Cu W	75/22/3	0.4	0.0007	0.0018
(9)	„ —Ni Fe Mo W	88/8/2/2	1.3	0.0003	0.0016
(10)	1/2 part by volume Raney-Ni 1/2 „ „ „ Ni/Cu/W as given under (8)		0.3	0.0005	0.0004

In test (10), the inlet half of the catalyst pot was filled with Raney nickel (2) as reduction catalyst, the outlet half of the catalyst pot being filled with the Raney metal alloy Ni/Cu/W mentioned under (8) as oxidation catalyst. Air at a rate of two litres per second was fed to the catalyst referred to under (8) by means of a group of pipes extending in

the direction of flow through the reduction bed.

WHAT WE CLAIM IS:—

1. An exhaust system for an internal combustion engine, the exhaust system having a catalyst in the path traversed in use by exhaust gases, the catalyst comprising one or more of the metals nickel, cobalt, iron, copper, silver, gold, chromium, molybdenum and tungsten, each such metal having been obtained by subjecting an alloy of it with an alloying metal to leaching with an acid or alkaline solution to remove said alloying metal.

2. An exhaust system according to Claim 1, in which the catalyst contains only one of said metals, said metal being nickel or copper.

3. An exhaust system according to Claim 1, in which the catalyst contains at least two of said metals one of which is nickel.

4. An exhaust system according to Claim 3, in which the catalyst comprises nickel and iron.

5. An exhaust system according to Claim 3, in which the catalyst comprises nickel, iron and copper.

6. An exhaust system according to Claim 3, in which the catalyst comprises nickel and copper.

7. An exhaust system according to Claim 3, in which the catalyst comprises nickel, copper and silver.

8. An exhaust system according to Claim 3, in which the catalyst comprises nickel and chromium.

9. An exhaust system according to Claim 3, in which the catalyst comprises nickel, copper and chromium.

10. An exhaust system according to Claim 3, in which the catalyst comprises nickel, iron, molybdenum and tungsten.

11. An exhaust system according to Claim 3, in which the catalyst comprises nickel, copper and tungsten.

12. An exhaust system according to any one of Claims 3 to 11, in which nickel is the main constituent of said metals by weight.

13. An exhaust system according to any one of the preceding claims, in which the catalyst is in the form of a double skeleton catalyst.

14. An exhaust system according to any one of the preceding claims, in which the catalyst comprises a layer less than 0.5 mm. thick.

15. An exhaust system according to Claim 14, in which the thickness of the catalyst layer is substantially 0.2 mm.

16. An exhaust system according to Claim 1, in which the catalyst has substantially the composition of any one of the catalysts (1) to (10) in the Example.

17. A method of reducing the content of noxious constituents in the exhaust gases of an internal combustion engine, which comprises passing the exhaust gases through the exhaust system claimed in any one of the preceding claims and in contact with the said catalyst.

EDWARDS EVANS & CO.,
53—64 Chancery Lane,
London, WC2A 1SD.
Agents for the Applicants.

Printed for Her Majesty's Stationery Office, by the Courier Press, Leamington Spa, 1975.
Published by The Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from which copies may be obtained.